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16. ABSTRACT

In order to assess the environmental impact of toxic chemicals in the United States, the Oak Ridge National Laboratory (ORNL) is developing a multimedia model to estimate the transport, diffusion, and removal of chemicals in the air-water-soil system. The Atmospheric Turbulence and Diffusion Laboratory (ATDL) was charged with assisting ORNL in the further refinement of the air transport and diffusion model and providing guidance on removal processes for toxic chemicals. This report is a review of the findings on removal processes. An overview is given of the general formulas and experiments regarding removal processes, Sections 3 and 4 contain specific removal methods for trace organic chemicals. Section 5 contains an application of the box model to simply account for all removal mechanisms discussed here. It soon became evident that there is disagreement among the experts regarding the quantitative estimation of removal of common pollutants, and nearly complete ignorance regarding specific organic chemicals. (Author extracted)

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A Progress Report to ORNL on Work Performed under the EPA
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1. INTRODUCTION

The Environmental Protection Agency is required to assess the environmental impact of toxic chemicals in the United States. They plan to screen these new chemicals in order to identify the more toxic ones for further study. Oak Ridge National Laboratory (ORNL) has agreed to develop a multimedia model to estimate the transport, diffusion, and removal of chemicals in the air-water-soil system. An important part of this study is the calculation of transfer rates from one medium to another; for example, the absorption of air pollutants by cloud water and subsequent removal by rain. Rain water then flows through streams, lakes, and soils.

Most air pollution eventually is removed from the atmosphere, either by transport to plants, soil, or water, or by chemical transformation to another compound. Rate of removal is governed by the chemical reactivity of the pollutant and characteristics of the environment, such as turbulent energy, relative humidity, and soil moisture content. There is a very wide range of observed removal rates, covering several orders of magnitude. Consequently, it is not easy to estimate removal rates for new toxic chemicals without the use of extensive field tests.

The Atmospheric Turbulence and Diffusion Laboratory (ATDL) was charged with assisting ORNL in the further refinement of their air transport and diffusion model and providing guidance on removal processes for toxic chemicals. This report is a review of our findings on removal processes. We begin with an overview in Sect. 2 of the general formulas and experiments regarding removal processes, and then move on in Sects. 3 and 4 to specific removal methods for trace organic chemicals. Section 5 contains an application of the box model to simply account for all removal mechanisms discussed here. It soon became evident that there is disagreement among

the experts regarding the quantitative estimation of removal of common pollutants, and nearly complete ignorance regarding specific organic chemicals.

2. A REVIEW OF REMOVAL PROCESSES FOR COMMON ATMOSPHERIC POLLUTANTS

2.2 Dry Deposition

The discussion on dry deposition is divided into sections for particles and gases. Large particles are removed by gravitational settling, and small particles are removed by impaction on the surface roughness elements.

2.2.1 Gravitational Settling

Particles with radii greater than about 5 μm have significant gravitational settling speeds. Stokes' law for the terminal settling speed v_t is valid for radii, r, less than 10 to 30 μm, depending on particle density:

$$v_t = \frac{2r^2 g\rho_p}{9\mu} \qquad (1)$$

where ρ_p is particle density, g is the acceleration of gravity, and μ is the dynamic viscosity of air (1.8×10^{-4} gm/sec cm). At larger radii, Stokes' law must be modified somewhat, and the graphical solution given by VanderHoven (1968) for spherical particles with density 5 g/cm^3 is plotted for sea-level situations in Figure 1. Settling speeds for particles with different densities ρ_p can be approximated by multiplying the speed in the figure by $(\rho_p/(5\text{g/cm}^3))$.

The settling speed of non-spherical particles can be calculated by dividing the speed of the equivalent sperical particle (equivalent radius $r_e = (3V_p/4\pi)^{1/3}$, V_p = particle volume) by a dynamical shape factor α. Typical shape factors are shown in Table 1 (Chamberlain, 1975).

Table 1

Dynamical shape factor α (Chamberlain, 1975)
(Ratio of terminal velocity of equivalent sphere to that of particle)

Shape[a]	Ratio of axes	α
Ellipsoid	4	1.28
Cylinder	1	1.06
Cylinder	2	1.14
Cylinder	3	1.24
Cylinder	4	1.32
Two spheres touching	2	1.10
Two spheres touching	2	1.17
Three spheres touching, as triangle	-	1.20
Three spheres touching, in line	3	1.34
Three spheres touching, in line	3	1.40
Four spheres touching, in line	4	1.58
Four spheres touching, in line	4	1.56

[a]In all cases, preferential motion is perpendicular to long axis.

Van der Hoven (1968) suggests that when v_t is greater than 100 cm/sec (radius $r \gtrsim 100$ μm), the particles are falling through the turbulence so fast that diffusion is no longer important. In this case, particle trajectories are calculated by a straightforward ballistics approach, based on the wind speed and the gravitational settling speed.

For v_t less than 100 cm/sec (radius $r \lesssim 100$ μm), it is assumed that the particles are dispersed by turbulence in the same way as inertialess particles. A plume model is used, but $h_g = xv_g/u$ is substituted for effective plume height h to account for gravitational settling. This is called the "tilted plume model" and is illustrated in Figure 2. Deposition of particles with $5 \text{ cm/sec} \lesssim v_t \lesssim 100 \text{ cm/sec}$ at the ground at any position x, y is given by the expression

$$\omega = v_t \, C \, (x, y, 0), \tag{2}$$

where ω is deposition rate in mass per unit area per unit time. In a Gaussian model of this situation, roughly half of the material is deposited by a distance hu/v_t, where the particle plume centerline strikes the ground. Thus for h equal to 100 m, u equal to 5 m/s, and 20 μm diameter particles with density 5 gm/cm^3 (v_t = 6 cm/s), about half the material is deposited within a distance of 8.3 km.

2.2.2 Deposition of gases and particles with radii less than about 10 μm.

Very small particles and gases are also observed to be deposited on surfaces, to which they are transported by turbulent diffusion and Brownian motion. Chemical absorption, impaction, photosynthesis, and other biological, chemical, and physical processes cause the material to be retained at the surface. In this case a deposition velocity, v_d, can be defined as an empirical function of the observed deposition rate, ω, and concentration near the surface, C_o:

$$v_d = \omega/C_o \tag{3}$$

The height at which C_o is measured is typically about 1 m. Once v_d is known for a given set of conditions, then the formula $w = v_d C_o$ can be used to predict dry deposition of gases and small particles, where C_o would be obtained from some appropriate diffusion model.

There are many methods available to incorporate dry deposition into existing effluent dispersion models; see Hosker (1980) for a survey. Even the relatively simple Gaussian plume model has been adjusted for dry removal by at least four techniques. The most common, and one of the easiest to use, is the so-called "source depletion" model in which the apparent strength of the source is allowed to vary with downwind distance to account for the diminishing amount of material remaining aloft. The rate of change of Q with distance is

$$\partial Q/\partial x = - \int_{-\infty}^{\infty} w(x, y)dy = - \sqrt{\frac{2}{\pi}} \frac{v_d Q}{u\sigma_z} e^{-h^2/2\sigma_z^2} , \qquad (4)$$

which leads to

$$Q(x)/Q(0) = \left[\exp \int_0^x \frac{dx}{\sigma_z \exp(h^2/2\sigma_z^2)} \right]^{-\sqrt{\frac{2}{\pi}} \frac{v_d}{u}} \qquad (5)$$

Graphical solutions to this equation using standard Pasquill-Gifford curves for σ_z are given by VanderHoven (1968). The resulting Q(x) is then used in place of the usual fixed source strength Q in the Gaussian plume equation. Table 2 uses Van der Hoven's graphs to estimate the downwind distance at which 50% of the plume is depleted for a wind speed, u, of 1.0 m/s and deposition speed, v_d, of 0.01 m/s.

Table 2

Distance at which 50% of Q is Depleted by Dry Deposition, as a Function of Pasquill Stability Class and Source Height. $u = 1.0$ m/s, $v_d = .01$ m/s.

Pasquill Class	Source Height 0 m	10 m	50 m	100 m
A and B	> 10 km			
C	1.8 km	18 km	43 km	60 km
D	0.4 km	3.5 km	8.6 km	19 km
E	0.15 km	2.2 km	8.3 km	17 km
F	0.10 km	2.0 km	10.0 km	28 km

Because of the $\exp(h^2/2\sigma_z^2)$ term in Eq. (5), the distance for 50% depletion in Table 2 is not always a continuously decreasing function of stability for any given source height. This model implicitly assumes that depletion occurs over the whole depth of the plume rather than at the surface; the plume's vertical profile is therefore invariant with distance.

A somewhat different approach has been summarized by Overcamp (1976) as the "partial reflection" model. In this instance, the "image" term in the Gaussian plume model is preceded by a reflection coefficient α, which is thus a fraction of the strength of the real source. This coefficient is determined by setting the deposition flux equal to the difference in fluxes from the real and image terms. The plume is also allowed to "tilt" to incorporate gravitational settling of large particles at terminal speed v_t:

$$C = \frac{Q}{2\pi\,\sigma_y\sigma_z u}\ \exp\left[-\frac{y^2}{2\sigma_y^2}\right]\left[\exp\left[-\frac{(z-h+v_t x/u)^2}{2\sigma_z^2}\right] + \alpha(x_G)\exp\left[-\frac{(z+h-v_t x/u)^2}{2\sigma_z^2}\right]\right] \qquad (6)$$

The reflection coefficient $\alpha(x_G)$ can be computed by solving an implicit relation for x_G,

$$\left[h - \frac{v_t x_G}{u}\right] \frac{\sigma_z(x)}{\sigma_z(x_G)} = z+h - \frac{v_t x_G}{u} \quad , \tag{7}$$

and the following equation for $\alpha(x)$:

$$\alpha(x) = 1 - \frac{2v_d}{v_t + v_d + (uh - v_t x)\sigma_z^{-1}(d\sigma_z/dx)} \quad . \tag{8}$$

In this model, dry deposition removes material from the lower portions of the plume, which therefore begins to show a non-Gaussian vertical concentration distribution. In unstable conditions, rapid mixing within the plume insures that the results from Eqs. (5) and (6) are not very different; in stable conditions, however, the flux to the surface estimated using Eq. (6) will be significantly smaller than Eq. (5) would suggest, especially far downwind.

Horst (1979) has compared the results of various deposition models. He concluded that, close to the source, the partial reflection model is the easiest to use, and is fairly accurate. Far downwind, however, the source depletion model performed better than the partial reflection model. He then suggested a modified version of the source depletion model which permits the plume vertical profile to vary with distance. It should be noted that field data to validate any dry deposition model are largely unavailable or inadequate (see Sehmel, 1980). Model selection is done mostly on the basis of the physical plausibility of the model's assumptions and predictions.

To operate any deposition model, a knowledge of the dry deposition velocity v_d is necessary. Both measured and theoretical estimates of v_d

are commonly used (Sehmel, 1980). Some theoretical models of deposition assume that the deposition process is analogous to electrical current flow across resistances. In effect, the deposition speed v_d is inversely proportional to the sum of an aerodynamic resistance to turbulent mass transfer, r_a, a resistance to transfer across the surface boundary layer, r_b, and a resistance to transfer into the surface, r_s. In principle, then, deposition speed should be a function of roughness length, friction velocity, and many other surface parameters. Wind tunnel data show clearly the dependence on roughness length and friction velocity. However, field measurements of deposition speeds contain much scatter and do not always agree with theories or with measurements in controlled laboratory environments. The values of v_d recommended in this chapter are based on reviews of field data by McMahon and Denison (1979) and Sehmel (1980). The interested reader can go to their reviews to find the original references. We arbitrarily assume that the field measurements are more reliable than theoretical estimates.

Figure 3 shows measured deposition speeds for particles to grass. For particles larger than about 1 μm, turbulent diffusion and gravitational settling are the dominant processes, while for particles smaller than 0.1 μm, Brownian diffusion becomes increasingly important. Theory and laboratory data indicate a minimum in v_d between 0.1 and 1 μm particle diameter; the exact value for v_d is predicted to depend on particle density, friction velocity u_*, and surface roughness z_o, among other things. Figure 4 shows typical calculated values. However, the scatter and sparsity of the field data preclude a vigorous validation of the expected behavior of v_d, although the general trends seem to be verified. The inaccuracies of the data suggest that, in any particular model calculation, one should use a <u>range</u> (often orders of magnitude) of possible v_d values, rather than a single estimate such as

the average. This will place upper and lower bounds on the computed deposition results, which is really all the accuracy that can be expected with the present state of the art. A few special cases are known to dramatically enhance the deposition rate. For example, deposition of particles to a forest canopy is measured to be about 2 to 16 times greater than that over open terrain, while mosses give rise to an order of magnitude increase in v_d. Special caution is warranted for unusual types of ground cover.

There are many measurements of v_d for gases reported by McMahon and Denison (1979) and Sehmel (1980). Biological and chemical activity play key roles in gaseous deposition, and may in fact provide the rate-limiting steps for deposition and uptake. For example, relatively inert gases such as CO typically have nearly negligible deposition speeds, 10^{-3} to 10^{-4} cm/s. If the gas is biologically or chemically active, however, the measured deposition speed is likely to be on the order of 0.5 to 3 cm/s. For example, a summary of SO_2 deposition speeds for various surface types is reproduced in Table 3, from Husar et al. (1978).

Table 3

SO_2 Deposition Rates from Husar et al. (1978)

Surface	v_d(cm/s)	Comment
Short grass	0.5	0.1 m height
Medium crop	0.7	1.0 m height
Calcareous soil	0.8	wet or dry
Acid soil	0.4	dry
Acid soil	0.6	wet
Dry snow	0.1	If wet, behaves like water
Water	0.7	
Countryside	0.8	
Cities	0.7	Based on London data only

Measurements in forests indicate no significant enhancement in v_d for SO_2 over that for grasses or crops. A dependence on wind speed cannot be discerned from the available data. It is found that during the night or the winter, when stomata are closed, v_d is about a factor of two to five less than during summer days.

The deposition speed of other reactive gases is found to be similar to that for SO_2. I_2 is deposited with a speed v_d averaging 1.5 cm/s, with relatively little scatter. Ozone is observed to be deposited with a speed v_d ranging from 0.02 to 1.4 cm/s, with an average value of 0.5 cm/s. The lowest ozone deposition speeds were observed over water and snow ($v_d \cong 0.1$ cm/s). Also, it appears that the ozone deposition speed is twice as large for neutral conditions as for unstable conditions. Many other experimental factors influenced the results, such as reference height, roughness, surface conditions, etc., but the data do not permit any quantitative conclusions regarding these factors.

2.3 Wet Deposition

The theoretical treatment of wet deposition is often divided into rainout (within-cloud scavenging) and washout (below-cloud scavenging). In practical applications the two processes are generally lumped together since they can be modeled similarly, although numerical values depend on the process (See the reviews by Hosker, 1980, or Slinn, 1981).

There are also two methods of modeling this problem. In the first, it is assumed that the concentration C decreases exponentially with time:

$$C(t) = C(0)e^{-\Lambda t} \tag{9}$$

where Λ is the so-called scavenging coefficient (time $^{-1}$) and t is time since precipitation began. The precipitation-induced flux of effluent to the ground is given by

$$F_{wet} = \int_o^{Z_w} \Lambda\, C\, dz, \tag{10a}$$

where Z_w is the depth of the wetted plume layer. For rain falling completely though a Gaussian plume,

$$F_{wet} = \frac{\Lambda Q}{\sqrt{2\pi}\,\sigma_y u} \exp\,(-y^2/2\sigma_y^2) \tag{10b}$$

The method is, strictly speaking, applicable only to particles of a single size ("monodisperse") and highly reactive gases which are <u>irreversibly</u> captured by the precipitation. Furthermore, the derivation of Eq. (9) involves the assumption that the scavenging coefficient is independent of both space and time. In modeling practice, however, Λ is often allowed to vary with position to account for changes in precipitation (and hence in scavenging rate) over the region of interest. The scavenging coefficient method <u>cannot</u> be applied directly to aerosols with a <u>range</u> of diameters ("polydisperse") unless an empirical value of Λ is available for particles of that type and size. In particular, one cannot apply a scavenging coefficient for an "average" particle whose size is equal to the geometric mean of the particle size range; the scavenging rate will be too small by more than an order of magnitude. Estimates of scavenging coefficients for polydisperse aerosols have been summarized by Dana and Hales (1976). The scavenging coefficient method is also <u>not</u> applicable to gases which are not highly reactive or which are merely soluble in water, since it

is essential in such cases to account for possible desorption of gas from droplets as they fall from regions of high effluent concentration (eg., an elevated plume) toward the ground (Hales, 1972). The case of soluble gases has been addressed by Hales et al. (1973) and Slinn (1974). Slinn finds that close to the source a Gaussian plume's shape is unaltered by the wet removal process, but the concentration dimishes exponentially with distance. Far from the source, the plume is "washed down" or "tilted" from its initial height by an amount dependent on the precipitation rate, droplet size, gas chemistry, wind speed, and distance downwind. The vertical dispersion parameter is also enhanced by an amount strongly dependent on droplet size by this process.

Other methods of modeling wet removal utilize the so-called washout ratio, W_r. Let k_o and C_o be the concentration of effluent in the precipitation (raindrops, say) and in the air, respectively, at some reference height; both quantities are measured in unit of mass/volume. Then

$$W_r \equiv k_o/C_o \quad . \tag{11a}$$

Other definitions are widely used (e.g., McMahon and Denison, 1979); let k_o' be the effluent concentration in the precipitation in terms of mass (e.g., mass of pollutant/unit mass of H_2O). The washout ratio in this case is written as

$$W' \equiv \rho_a k_o'/C_o \quad , \tag{11b}$$

where ρ_a is the density of air ($\tilde{\sim}$ $1.2\text{X}10^{-3}$ g/cm^3). The dimensionless ratios are related by

$$W' = \frac{\rho_a}{\rho_w} W_r \quad , \tag{11c}$$

where ρ_w is the density of water ($1 g/cm^3$). Thus W_r is almost 1000 times larger than W'; since both definitions (11a) and (11b) are common in the literature, the user must be careful. The following discussion will utilize W_r, for convenience.

The flux of effluent to the surface as a result of the precipitation is just

$$F_{wet} = k_o J_o \tag{12}$$

where J_o is the equivalent rainfall rate in, say, mm/hr. If W_r is known and the concentration in air C_o can be measured or estimated from a plume model, then

$$F_{wet} = C_o W_r J_o \quad . \tag{13}$$

The washout ratio can also be used to define a wet deposition velocity by analogy to the dry:

$$v_w \equiv F_{wet}/C_o = W_r J_o \tag{14}$$

This can then be used like v_d to develop models for the wet scavenging process. Analysis (summarized in Hosker, 1980) of the microphysics of the wet scavenging process yields an approximate relationship between the scavenging rate and washout ratio:

$$\Lambda \tilde{\approx} W_r J_o / Z_w \tag{15}$$

where Z_w is the depth of the wetted plume layer. Hence the washout ratio can also be used in exponential decay models of wet plume depletion (Eq. 9).

The scavenging coefficient Λ is theoretically a function of droplet size spectrum, physical and chemical characteristics of the particle or gas, and precipitation rate. McMahon and Denison (1979) report 20 field experiments in which Λ was measured for particles, giving a median value of Λ of 1.5×10^{-4} sec^{-1} and a range from 0.4×10^{-5} sec^{-1} to 3×10^{-3} $sec.^{-1}$. They find washout and rainout coefficients are nearly equal, and do not find systematic differences in Λ as particle size or rain characteristics change. Their median value of Λ for SO_2 is about 2×10^{-5} sec^{-1}, and one laboratory experiment showed that $\Lambda = 17 \times 10^{-5} J_o^{0.6}$, where J_o is rainfall in mm/hr. A value of Λ ranging from 10^{-5} to 10^{-4} sec^{-1} implies a half life for wet removal processes ranging from about two hours to one day. The use of scavenging coefficients for wet removal modeling is probably best regarded as an order of magnitude estimation procedure. This is particularly true if empirical values of Λ are unavailable or inappropriate for the conditions at hand, so that theoretical estimates of Λ must be used. The procedure is most useful for single episodic events, where the available theory does permit some adjustment for the peculiarities of individual storms.

There are many field observations of washout ratio, W_r, which can be determined by measuring pollutant concentrations in air and in rainwater. It is observed to decrease with precipitation amount during any given experiment presumably because the pollutant cloud becomes more dilute. On the average, W_r decreases by a factor of two for each order of magnitude increase in rainfall. Over half of the washout ratios W_r reported by McMahon and Denison (1979) are in the range from 3×10^5 to 10^6 with a median of about 6×10^5. There may be some variation with pollutant type, although the ranges in observed W_r for different

pollutants generally overlap each other and no statistically significant differences can be proven. The use of washout ratios is probably best suited to long-term estimates, where the variability induced by single storm events is integrated out.

2.4 CHEMICAL REMOVAL

Primary pollutants are those that are emitted directly into the atmosphere, such as SO_2, CO, and NO_2. Secondary pollutants are those that are created through chemical reactions involving the primary pollutants. For example, sulfates form when SO_2 is oxidized, or ozone is formed when a mixture consisting of NO_2, NO, and reactive hydrocarbons is subjected to sunlight.

Often an exponential chemical decay rate is assumed with time constant T_c:

$$C(t)/C(0) = e^{-t/T_c} \tag{16}$$

Conversion from SO_2 to sulfate is often treated as an exponential process, but there is much debate over the proper value for the time constant T_c. The reaction rate depends on humidity and the presence of catalysts, and so T_c has been measured to range from an hour to several days. A typical value of T_c used in long range transport models is about four days.

Chemical removal can also be studied by using the kinetic equations. For example, assume that the following two chemical kinetic equations are valid:

$$A + B \xrightarrow{k_1} D \tag{17}$$

$$D + E \xrightarrow{k_2} A \tag{18}$$

where k_1 and k_2 are rate constants (concentration^{-1} time^{-1}). Then the rate of change of concentration of substance D due to chemical reactions is given by the equation:

$$dC_D/dt = k_1 C_A C_B - k_2 C_D C_E \tag{19}$$

When the continuity equation for substance D is written, this term should be added to the diffusion terms on the right hand side. Equation (19) is often used in the analysis of photochemical smog. The set of chemical kinetic equations for photochemical smog is in a continual state of development, with the latest model (Falls and Seinfeld, 1978) utilizing 55 equations. A rough picture of the formation of smog is given in Fig. 5. Primary emissions consist of hydrocarbons, NO, and some NO_2. Sunlight (hv) results in the formation of free radicals and the ultimate production of the problem pollutants ozone (O_3) and PAN.

3. SPECIFIC METHODS OF ACCOUNTING FOR ATMOSPHERIC REMOVAL OF TOXIC CHEMICALS

It is popular among reviewers these days to point a pessimistic view of our knowledge of atmospheric removal processes, even for common substances (see Sehmel, 1980). These authors point out the wide range of observed

values of, for example, deposition velocity for SO_2, and hesitate to make recommendations. The review by McMahon and Denison (1979) used extensively in the last section, is one of only a few that take a positive approach and recommend values of parameters for use in applied studies. To operate the EPN ORNL Multi-Media Model, it is essential that specific values be assigned to parameters such as the dry deposition velocity or the washout ratio.

The current literature on atmospheric removal of organics is one or two orders of magnitude smaller than the literature on removal of sulfur compounds. Most of the recent work is in the so-called "gray" area of conference proceedings and local reports. For example, we will draw heavily on a workshop report (Miller, 1980) entitled "The Potential Atmospheric Impact of Chemicals Released to the Environment," which was prepared for the EPA Office of Toxic Substances. In addition, several relevant papers concerning deposition to water were presented at the 1979 Meeting of the Division of Environmental Chemistry of the American Chemical Society.

To make gross estimates of the wet and dry deposition of organic chemicals, it is necessary to know the air concentration, the rainfall rate, the dry deposition speed, and the washout ratio. Then Eqs. (2) and (12) can be easily applied. In the rest of this ection, measures of dry deposition speed and washout ratio are emphasized.

3.1 Deposition of Trace Organic Chemicals to Land

Atmospheric transport of harmful organic chemicals such as DDT and PCB's is known to result in accumulations of these chemicals in remote regions of the world far away from the sources. It is expected that the

same would be true of new organic chemicals that are proposed. Junge (1977) concludes that most of the PCB's and DDT are in the vapor phase rather than being absorbed onto a water drop or a particle, but most observations of deposition cannot distinguish among the phases. Measured dry deposition velocities for several organic species are summarized by Miller (1980), whose table is reproduced here as Table 4. The observed v_d is calculated as the ratio of the observed deposition on a special surface to the air concentration above the surface. The v_d's in the table range from 0.04 to 1.3 cm s^{-1}, with a median value of 0.5 cm s^{-1}. These values are close to those reported by McMahon and Denison (1979) for a variety of inorganic chemicals.

Table 4. Measured deposition speeds, $v_d = w/C$, for several trace atmospheric organic compounds (Miller, 1980)

Compound	Deposition speed, v_d
PCB (Aroclor 1242,1254)	0.5 cm/sec
PCB's	0.3-3 cm/sec
PCB's, DDT	0.19 cm/sec
PCB's, DDT	1.0 cm/sec
PCB's (total)	0.14 cm/sec
PCB's (Aroclor 1015)	0.04 cm/sec
PCB's (Aroclor 1254)	0.43 cm/sec
Chlordane	0.068 cm/sec
p, p-DDT	1.3 cm/sec
Toxaphene	0.24 cm/sec

3.2 Deposition of Trace Organic Chemicals to Water

After a long enough time, the concentrations of a substance in water and air will reach a chemical equilibrium at the interface. This is a steady state condition that the system approaches asymptotically. At equilibrium, Henry's constant, H, is defined by chemists by the following ratio:

$$H(\text{atm}\cdot\text{m}^3.\text{mol}) = P(\text{atm}\cdot\text{partial pressure})/$$
$$S(\text{g mol}/\text{m}^3, \text{ water concentration at equilibrium}) \quad (20)$$

The parameter S is commonly called the solubility. McKay et al. (1979) outlines a method for measuring H, and McKay (1979) provides a nomogram, reproduced as Fig. 5 in which Henry's constant for many organics is given. To estimate H for a new organic chemical, it should be possible to use H from this figure for the substance most closely related to the new chemical. McKay (1979) suggests the following empirical formula for the "half life" T of a pollutant in the air over "clean" water:

$$T = 29L(20000H + 2.4) \quad (21)$$

where T is in seconds, L is the effective atmospheric depth (McKay assumes L = 100 m), and Henry's constant H has the units given in Eq. (20). To illustrate the use of this technique, pick ethylene dichloride on Fig. 5. Henry's constant H is 10^{-3} atm·m^3/mol and Eq. (21) gives a half life T equal to 6.5×10^4 sec, or about 18 hours. In other words, the air concentration of ethylene dichloride will decrease exponentially such that 50% of the chemical is absorbed by the water in 18 hours.

The above procedure was developed by chemists and assumes that both the air and water are well-mixed. Fluid dynamicists take a different approach and look at the turbulent transfer of chemicals in the air and water layers and at their interface (Slinn et al., 1978). This approach introduces new complications based on limited observations of natural water surfaces. For example, Blanchard and Packer (1979) find that

much of the transfer at the interface is due to breaking waves and bubbles on the water surface. Elzerman (1976) and Meyers and Owen (1979) observe that the concentration gradient in the water near the surface is very large, such that "enrichment" of the surface microlayer is typically a factor of five to ten. Think of the organic slime seen on the surface of many water bodies. This surface enrichment could affect the absorption of organics by a water surface. Williams (1979) has measured the dry deposition of particles and gasses to water and concludes that the rate governing processes occur at the surface. Unfortunately, this research area is in its infancy and well-validated theories are not yet available.

A few observations of the deposition of organics to water are available. Eisenreich et al. (1979) and Murphy and Rzeszutko (1977) measured PCB deposition in Lakes Superior, Huron, and Michigan, and concluded that most of the PCB in the lakes is due to atmospheric deposition. They derived a dry deposition speed, v_d, of 0.15 cm s^{-1}. Bidleman (1979) found deposition speeds ranging from 0.6 to 1.6 cm s^{-1} for five chlorinated hydrocarbons in coastal South Carolina. The deposition speed was observed to increase slightly with wind speed. A comprehensive experiment is badly needed in which the deposition speed was observed to increase slightly with wind speed. A comprehensive experiment is badly needed in which the deposition speed of organics to water is measured for a variety of atmospheric condition and water surface conditions.

3.3 Washout of Trace Organic Chemicals

At least as much trace organic material is removed from the atmosphere by washout as by dry deposition (Miller, 1980). Wet removal proceeds through both scavenging of organic particles and absorption of organic gasses by cloud and rain drops. Slinn et al. (1978) estimate that a typical drop will reach equilibrium with an organic gas before the drop has fallen 10 m. Consequently, Henry's constant can be used to estimate the concentration of trace organics in the raindrop. The scavenging ratio W [Eq. (9)] is inversely proportional to Henry's constant [Eq. (18)]:

$$W = \frac{m}{10^6 H} \tag{22}$$

where m is the molecular weight (g/mol) of the chemical and H has units ($atm \cdot m^3/mol$). Experimental values of H for organic chemicals measured by McKay et al. (1979) range from 3.9×10^{-5} for phenanthrane to 6.6×10^{-3} for toluene. Data presented by Miller (1980) suggest that theoretical and observed values of H can differ by several orders of magnitude for various types of PCB's. It is therefore recommended that observed rather than theoretical H values be used. Unfortunately, this ideal situation may not be possible in the time frames available for EPA evaluation of the environmental impact of chemicals.

4. CHEMICAL REMOVAL OF ATMOSPHERIC ORGANIC CHEMICALS

The basic equations for chemical removal were reviewed in Sect. 2.4. A number of organic species are reactive in the presence of sunlight and

other typical urban polltants. Cox et al. (1980) conducted photo-oxidation experiments with several organic chemicals, resulting in evaluation of relative rate constants for the reaction of OH with these chemicals. In most cases, the reaction with OH is rate-limiting. They found that the formulas

$$C(HC)/C_0(HC) = e^{-kC(OH)t} = e^{-\tau/T_R} \qquad (23)$$

provided a good fit to their data, where $C_o(HC)$ is the initial concentration of the organic chemical, k is the rate constant, and T_R is the time scale for removal defined by $T_R = 1/kC(OH)$. The mixture consisted of nitrous acid (HONO) and the organic chemical being studied, and the lighting system consisted of flourescent lamps. Concentration of OH remained constant (5×10^7 molecules/cm^3) is all experiments. Time constants observed in this experiment are given in Table 5 for several organic chemicals. It is seen that, at these OH concentrations, time constants range from a few minutes to a few hours, implying that chemical removal of organic species is a very important removal mechanism.

Time scales for other OH concentrations can be estimated from Table 5 using the relation $T_{R2}/T_{R1} = C_1(OH)/C_2(OH)$, assuming that $C_1(OH)$ equals 5×10^7 hydroxyl radicals/cm^3, as used in the experiments leading to Table 5. Therefore, to know the time constant for an organic chemical, it is necessary to know the OH concentration. In and urban area, typical observed smog concentrations and state-of-the-act multistep chemical kinetic mechanisms can be used

Table 5. Time Constants for Reaction of Selected Organic Species with OH (Cox et al., 1980). Constant OH concentration = 5×10^7 hydroxy radicals/cm^3; Constant Lighting Intensity

Compound	Time constant T_R (min)
Olefins	
Ethylene	36
Propene	12
Isoprene	4
Cyclohexene	5
Aromatics	
Bensene	360
Toluene	40
0-xylene	22
m-xylene	15
Ketones	
Acetone	576
Methyl ethyl ketone	111
Methyl isobutyl ketone	23
Methyl vinyl ketone	21
Paraffins	
Propane	152
n-pentane	58
Isopentane	82
2-methylpentane	58
2, 3-dimethylbutane	76

to estimate C(OH). But in a rural area, background concentrations of photochemical pollutants are less well-known and a detailed photochemical model based on measured emissions and meteorological conditions should be applied. These techniques are probably beyond practicality for the EPA problem of assessing the impact of chemicals. With so many sub-modules in the multimedia model, it is not wise to overanalyze one particular detail. Instead, we should assign urban, suburban, and rural time constants for each new chemical based on the time constants for the organic chemical in Table 5 whose chemical characteristics are closet to those of the new chemical.

5. AN ATMOSPHERIC BOX MODEL FOR USE IN SCREENING PROCEDURES

A simple box model is often useful for screening chemicals in order to estimate which ones are likely to present environmental problems. In this box model, concentrations C is assumed to be uniform across a region of along-wind width Δx and depth z_i. We can account for removal processess in this model by using the definitions in previous sections:

$$\text{dry deposition removal} = -v_d A \Delta x$$

$$\text{precipitation scavenging} = -\Lambda C \Delta x z_i$$

$$\text{chemical removal} = -(C/T_c)\Delta x z_i$$

If a steady state and no upwind background are assumed, the continuity equation for this box becomes:

$$\Delta x Q_a - uz_i C - v_d C \Delta x - \Lambda C \Delta x z_i - (C/T_c)\Delta x z_i = 0 \qquad (24)$$

source	advection loss	dry deposition loss	precipitation loss	chemical loss

The solution is:

$$C = \frac{Q_a \Delta x / u z_i}{1 + \frac{v_d}{z_i}\frac{\Delta x}{u} + \Lambda \frac{\Delta x}{u} + \frac{1}{T_c}\frac{\Delta x}{u}} \qquad (25)$$

The numerator of Eq. (17), $Q_a \Delta x / u z_i$, is the steady state box model solution in the absence of removal processess. The terms in the denominator all act to decrease the concentration. Realizing that $\Delta x/u$ is the flushing time for the box, then all these correction terms can be thought of as the ratio of the flushing time to the characteristic removal time scale for that process. The smaller the removal time scale, the greater the ratio and the less the concentration C. Typical values of the parameters in this equation are:

$v_d = .01$ m/s $\qquad \Lambda = 10^{-4}$ s^{-1} $\qquad T_c = 10^4$ s

$\Delta x = 2 \times 10^4$ m $\qquad u = 5$ m/s $\qquad z_i = 500$ m

These parameters might be used for urban SO_2 pollution on a rainy day. The denominator in the equation for this set of parameter in thus 1.88, implying that the concentration is almost a factor of two less than that given by the simple box model with no removal processes. This model permits estimation of the dry or wet deposition flux to the water or soil surface, for use as input to hydrological or soil transport models.

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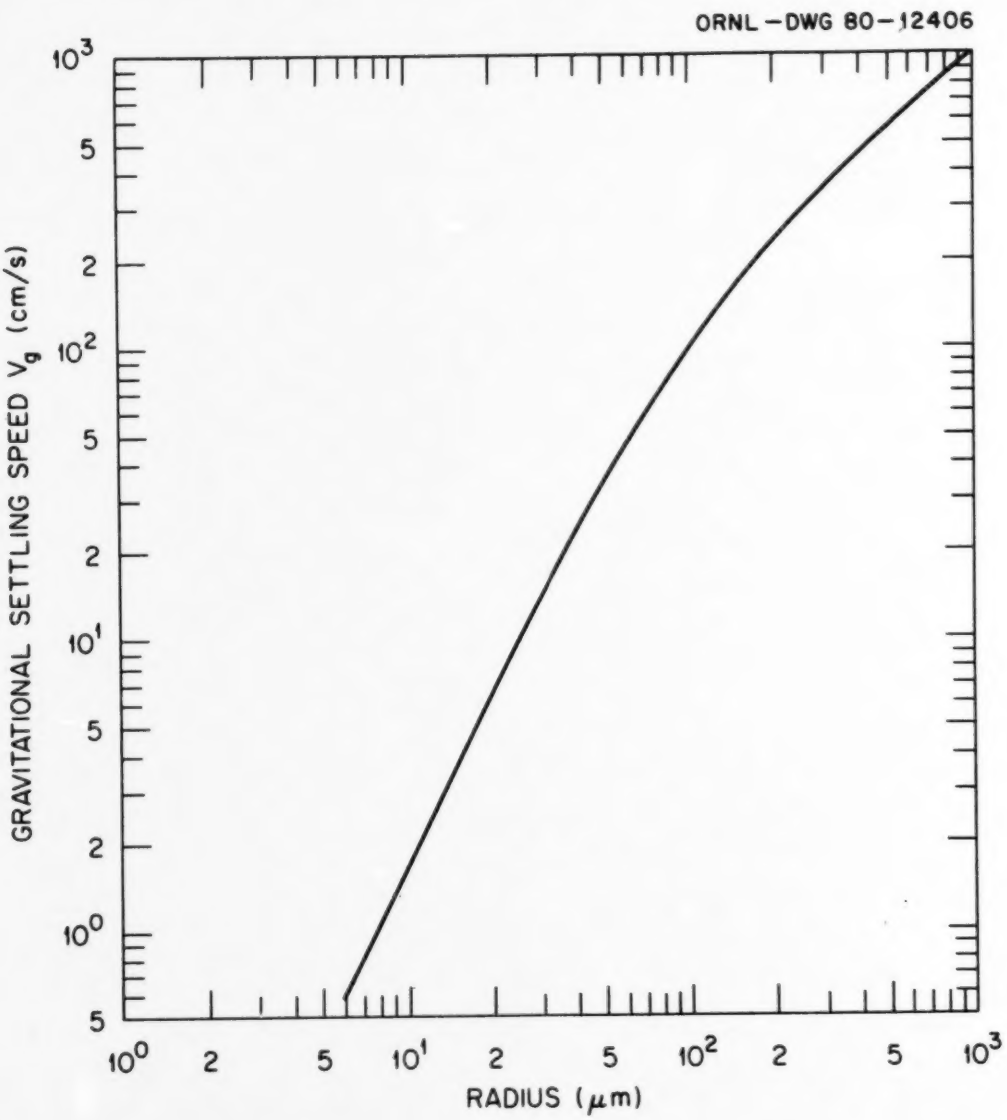

Figure 1. Gravitational settling speeds for particles with density 5 g/cm^3 near the earth's surface (from Engelmann, 1968).

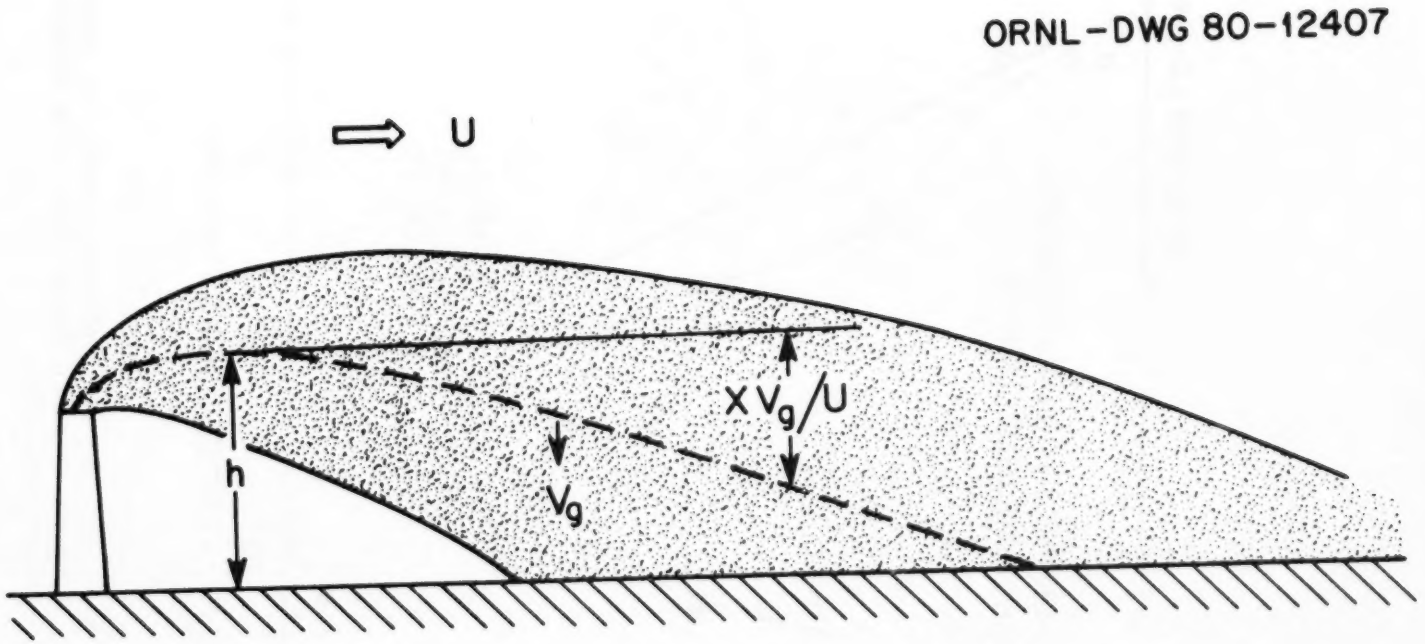

Figure 2. Tilted plume model. The plume axis drops with

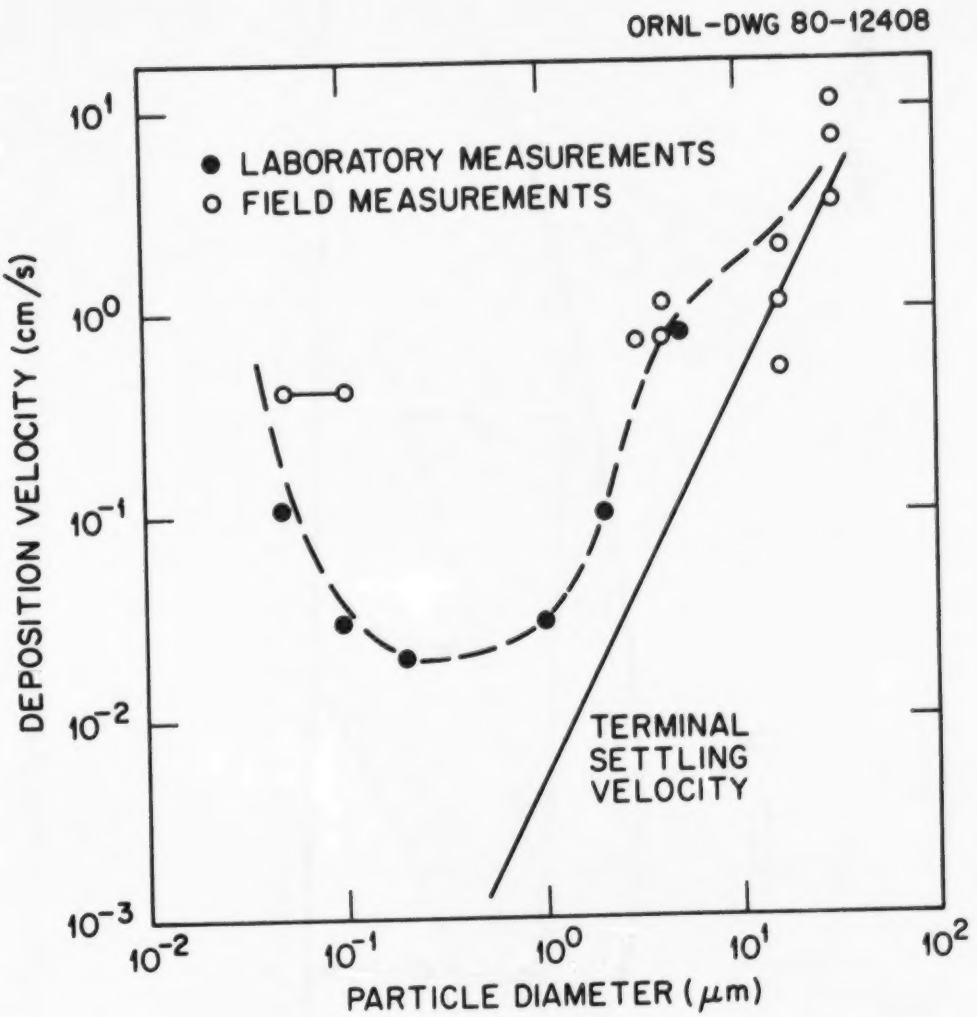

Figure 3. Laboratory and field measurements of deposition speeds of particles to grass (from McMahon and Dennison, 1979).

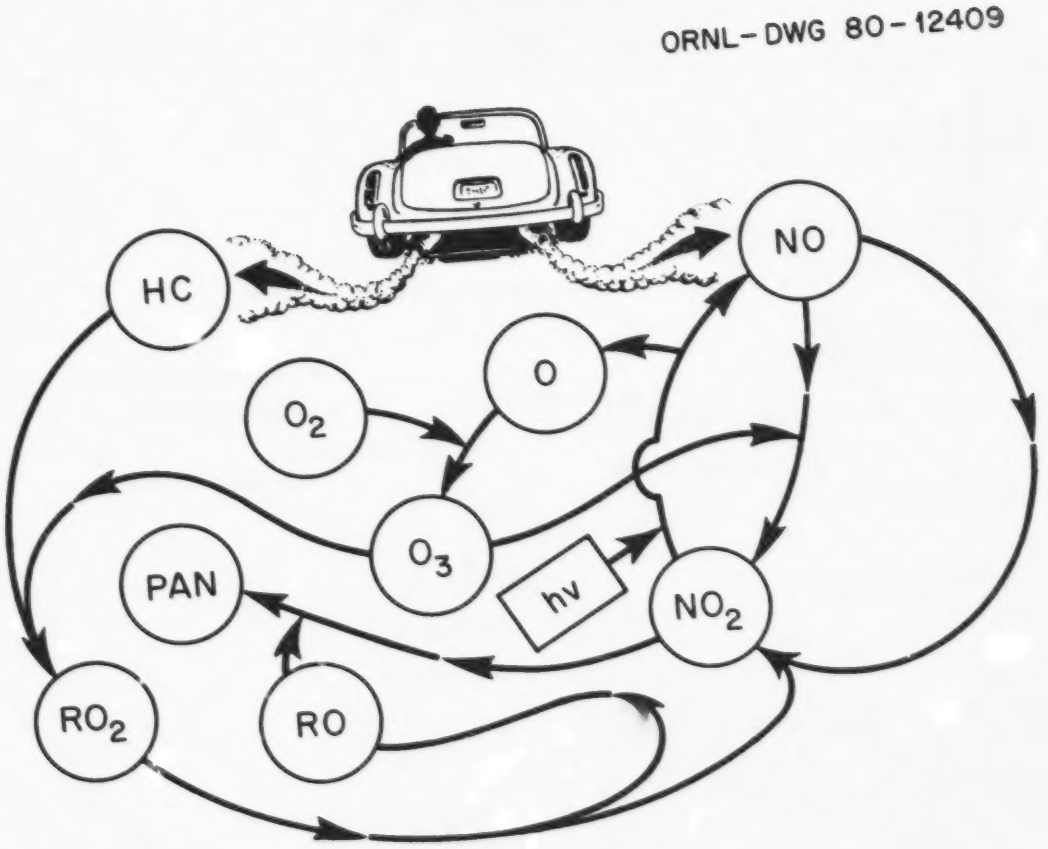

Figure 4. Simplified diagram of photochemical smog reactions. hν is the energy of a photon (from sunlight) and R is a free radical.

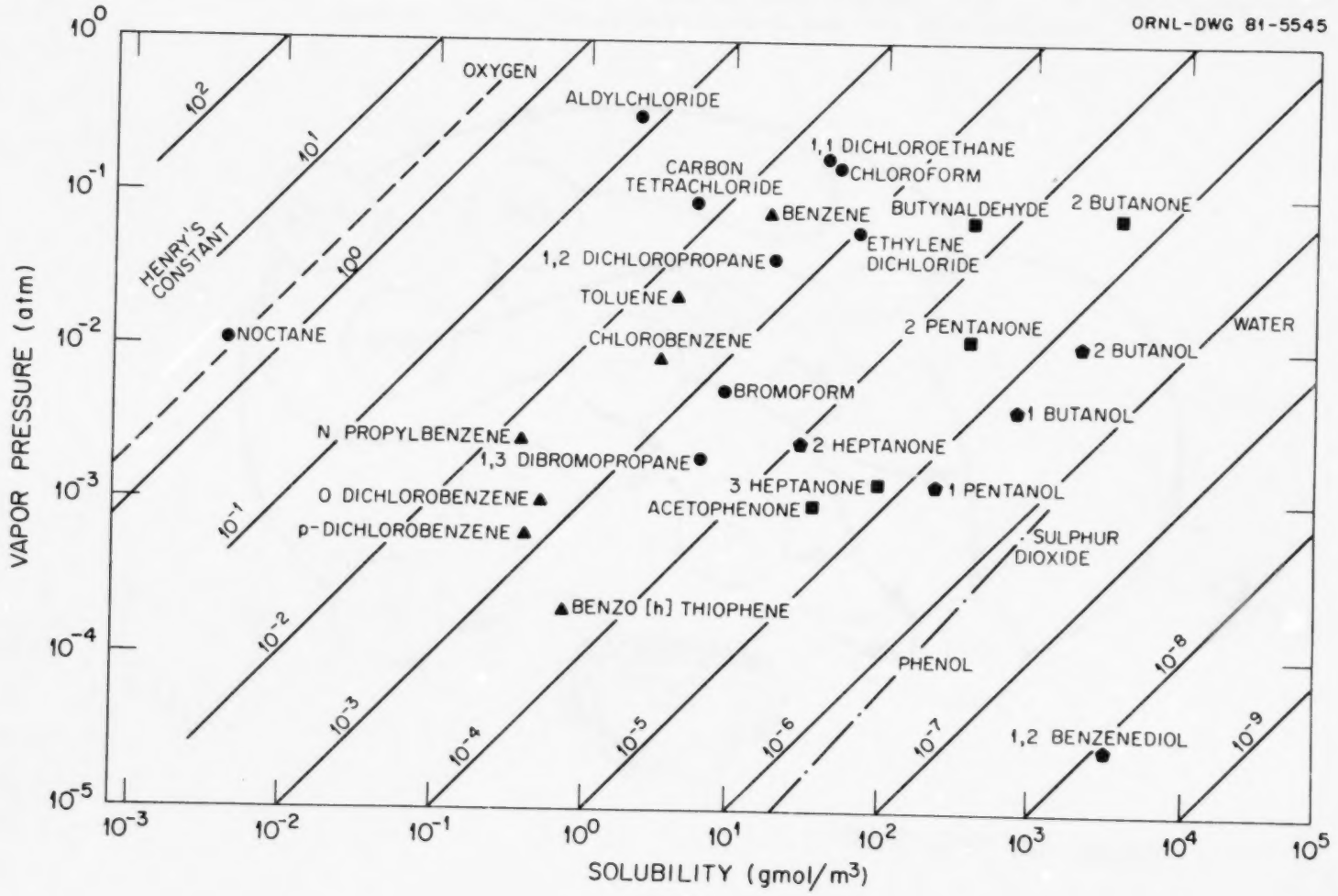

Figure 5. Plot of solubility, vapor pressure and Henry's constant (20°C) (McKay, 1979).